



# Room-temperature catalytic oxidation of benzo(a)pyrene by Ce-SBA-15 supported active $\text{CeSiO}_4$ phase

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## ABSTRACT

A series of cerium-incorporated SBA-15 mesoporous materials were prepared through direct hydrothermal synthesis method, which was characterized by PXRD,  $\text{N}_2$  physisorption and TEM measurements. The low-angle PXRD and  $\text{N}_2$  physisorption results show the cerium successfully incorporated into the framework of SBA-15. The large angle PXRD results indicate that Ce-SBA-15 mesoporous materials supported  $\text{CeSiO}_4$  phase was in situ synthesized by adjusting pH to 6 with anhydrous triethylamine, and then calcined in air at 550 °C. The room-temperature adsorption behaviors of SBA-15 and Ce-SBA-15 materials for benzo(a)pyrene in cyclohexane solutions were investigated. Interestingly, Ce-SBA-15 materials reveal good catalytic performance for room-temperature oxidation benzo(a)pyrene to corresponding quinone through a radical oxidation mechanism, attributable to in situ forming active  $\text{CeSiO}_4$  phase which was supported in Ce-SBA-15 material. The benzo(a)pyrene transfer to quinone by  $\text{CeSiO}_4$  phase leads to higher adsorption capacity owing to higher affinity of quinone with mesoporous channels, as a result, some Ce-SBA-15 materials exhibit higher adsorption capacity for benzo(a)pyrene than SBA-15 material. The radical oxidation mechanism was demonstrated by EPR and the interception effect of a radical scavenger, TEMPO. The quinone-type molecule was identified by photoluminescence, ESI-MS, IR and NMR.

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## 1. Introduction

Reducing the emissions of toxic substances such as POPs (persistent organic pollutants) has received special attention for the last 10 years [1]. The POP's family includes polychloro-dibenzodioxins (PCDDs also called dioxins), polychloro-dibenzofurans (PCDFs also called furans), polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs). Their presence in the environment is harmful to humans but also to the ecosystems. In particular, the release of PAHs has started to cause considerable concern. Most PAHs stem from the atmospheric deposition and diesel emission which are mainly emitted during the incomplete combustion of organic matters, such as diesel, gasoline, biomass, coal and wood [2–4]. PAHs are listed as carcinogenic and mutagenic priority pollutants, belonging to the environmental endocrine disrupters. Consequently, the elimination of PAHs is one of the priority and emerging challenges.

A series of different technologies has been developed to reduce PAH emissions including biodegradation, absorption, adsorption, high-energy electron beam, ozonization and catalytic oxidation [5–8]. Among them, catalytic oxidation of PAHs has been

demonstrated to be one of the most promising and cost-effective technologies for the removal of PAHs due to the lower combustion temperatures required and the higher selectivity toward  $\text{CO}_2$  [9,10]. Noble metal based catalysts, such as Pt and Pd supported on different metal oxides, are very active for the removal of PAHs, especially naphthalene [11–13]. However, the development of more active and cost-effective catalysts for the complete oxidation of PAHs remains a major research target. Among an extensive range of metal oxide catalysts, it has been demonstrated that  $\text{CeO}_2$  were significantly more effective catalysts for the treatment of PAHs emissions, especially naphthalene [14–17], attributable to the  $\text{Ce}^{3+}/\text{Ce}^{4+}$  redox cycle which leads to high catalytic activity of  $\text{CeO}_2$  [5].

Mesoporous SBA-15 has attracted great attention due to its highly ordered hexagonal structure with larger pore diameter, narrow pore size distribution, thick pore wall and high surface areas. However, the pure silica mesoporous SBA-15 has been seldom used as catalyst because of its lack of sufficient acidity and redox properties. The cerium-containing SBA-15 (Ce-SBA-15) materials obtained by the direct hydrothermal method have been reported [18–20]. These cerium-containing SBA-15 materials possessed the typical hexagonal structure of SBA-15, and displayed a large pore diameter and a higher specific surface area than SBA-15 [18]. These cerium-containing SBA-15 materials also show good catalytic activities, such as oxidative of cyclohexane [20], oxidative cleavage of cyclohexene [21]. Moreover, it was found that the mesoporous

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Ce-SBA-15 supported metal catalysts also exhibit good catalytic performance. The effect of cerium on the activity of Cr-SBA-15 catalyst in oxidative dehydrogenation of ethane to ethylene was investigated [22]. It was found that adding Ce species to Cr/SBA-15 catalysts remarkably changed the redox properties and enhanced the catalytic activity of chromium species in catalysts. Ce-SBA-15 supported cobalt catalyst possesses high catalytic activity in the oxidation of benzene [23]. Zr–Ce-SBA-15 supported palladium catalysts can be used for toluene catalytic oxidation [24]. Ce-SBA-15 supported nickel catalysts exhibit good catalytic performance for methane dry reforming to hydrogen and syngas [25].

Very recently, metal ions incorporating mesoporous materials or mesoporous materials supported metal catalysts showed higher activity for catalytic oxidation of naphthalene [26–30], because mesoporous materials generally exhibit diverse applications, especially catalysis [31–33]. SBA-15 impregnated with  $\text{CeO}_2$  was reported to obviously enhance catalytic activity and stability of catalysts for steam reforming of methane, which was due to that  $\text{CeO}_2$  layer precoated on SBA-15 [34]. We have discovered that cerium-incorporating mesoporous silica can selective reduction of bulky PAHs from mainstream smoke of cigarettes [35]. In this work, we report the hydrothermal synthesis of cerium-incorporating SBA-15 by co-templating method. It is found that one active phase ( $\text{CeSiO}_4$ ) was in situ formed in Ce-SBA-15 materials. Also, we discover for the first time that adsorbed benzo(a)pyrene (BaP) on Ce-SBA-15 can be oxidized to corresponding quinone at room temperature by active  $\text{CeSiO}_4$  phase supported on Ce-SBA-15.

## 2. Experimental

### 2.1. Materials and methods

All reagents were commercially available and used without further purification. FT-IR spectrum (KBr disk,  $4000\text{--}400\text{ cm}^{-1}$ ) was recorded on Bruker EQUINOX55 FT-IR spectrophotometer.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were obtained on Bruker Avance 400 MHz NMR spectrometers using  $\text{CDCl}_3$  as solvent and tetramethylsilane (TMS) as the internal standard. The powder X-ray diffraction (PXRD) patterns of the samples were collected on a Philips X'Pert PRO SUPER diffractometer operating with nickel-filtered  $\text{Cu-K}\alpha$  radiation ( $\lambda = 1.540598\text{ \AA}$ ) at 40 kV and 200 mA. The diffractograms were recorded in the  $2\theta$  range of  $0.8\text{--}10^\circ$  (low-angle) and  $10\text{--}70^\circ$  (wide-angle). Transmission electron microscopy (TEM) images were taken on a JEOL 2010 electron microscope operating at 200 kV. Nitrogen sorption and desorption isotherms were measured at  $-196^\circ\text{C}$  with a Micromeritics ASAP 3020 analyzer (Micromeritics, USA). Before measurements, samples were degassed in a vacuum at  $200^\circ\text{C}$  for at least 5 h. The Brunauer–Emmett–Teller (BET) method and the Barrett–Joyner–Halenda (BJH) model were utilized to calculate the specific surface areas (BET), the pore volumes and pore size distributions, respectively. The total pore volumes ( $V_t$ ) were estimated from the adsorbed branch at a relative pressure  $P/P_0$  of 0.994. The solution photoluminescence (PL) spectra were determined at room temperature on a Fluorolog-3-TAU fluorescence spectrophotometer. The EPR spectra were recorded on a JES-FA 200 ESR spectrometer at X-band. Electrospray ionization mass spectra (ESI-MS) were obtained using a LCQ Advantage Max mass spectrometer (Finnigan, San Jose, CA, USA). The BaP concentrations were analyzed by HPLC–FLD (Agilent 1100) with  $\lambda_{\text{ex}} = 297\text{ nm}$  and  $\lambda_{\text{em}} = 405\text{ nm}$ .

### 2.2. Synthesis of SBA-15 and Ce-SBA-15 materials

In a typical synthesis: 2.7 g of tri-block copolymer pluronic P123 ( $\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$ ) was dissolved in 20 mL of  $\text{H}_2\text{O}$  to get a clear solution. Thereafter, 1.683 g of NaCl and 50 mL 0.29 mol/L

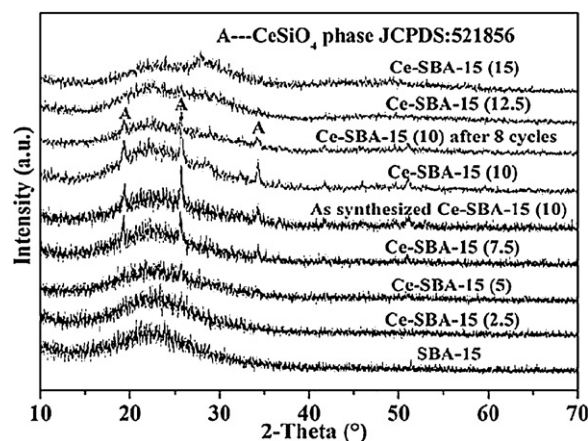


Fig. 1. PXRD patterns at high angle for SBA-15 and Ce-SBA-15 samples.

of HCl were added, and the solution was stirred at  $40^\circ\text{C}$  for 4 h. Then, 5 g of tetraethylorthosilicate (TEOS) and various amounts of  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (the Ce/Si molar ratio of 0, 2.5, 5, 7.5, 10, 12.5 and 15%) were added, and the resulting mixture was stirred at  $40^\circ\text{C}$  for another 20 h. Thereafter, pH value of reaction system was adjusted to 6 using anhydrous triethylamine (TEA), and resulting gel was placed into a Teflon-lined stainless autoclave. The autoclave was sealed and heated at  $100^\circ\text{C}$  for 24 h. The resulting solid was collected by filtration and washed with ethanol, and then dried at  $100^\circ\text{C}$  overnight. Finally, the solid was calcined in air at  $550^\circ\text{C}$  (heating rate  $2^\circ\text{C}/\text{min}$ ) for 5 h.

### 2.3. Adsorption of BaP

The adsorption BaP was performed by introducing, under shaking at room temperature for 6 h, 20 mg of the mesoporous material in a 10 mL cyclohexane solution containing different initial concentrations of BaP. Thereafter, the solid was separated by filtration using a  $0.45\text{ }\mu\text{m}$  Millex-GVMilli pore filter, and the filtrate was analyzed by HPLC–FLD, in order to calculate adsorption capacity.

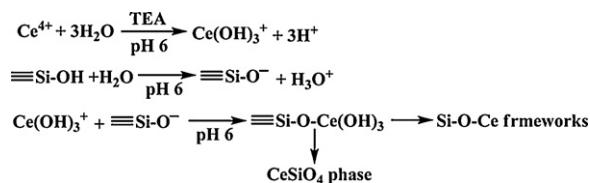
### 2.4. Extraction of quinone

The in situ forming quinone was eluted by methanol, 100 mg of BaP-adsorbed mesoporous material with 10 mL methanol. Thereafter, the separated solid was finally dried at  $150^\circ\text{C}$  under vacuum condition for recycling experiment. To obtain required amount of quinone, many times experiments were done according to the above process. The combined filtrate was evaporated to dryness under reduced pressure at  $50^\circ\text{C}$ , and then used to carry out PL, IR,  $^1\text{H}$  and  $^{13}\text{C}$  NMR and ESI-MS determination.

## 3. Results and discussion

### 3.1. Syntheses

The SBA-15 was prepared according to a procedure described in literature [36]. According to various Ce/Si molar ratios (2.5, 5, 7.5, 10, 12.5 and 15), the synthesized Ce-SBA-15 materials were named as Ce-SBA-15 (2.5), Ce-SBA-15 (5), Ce-SBA-15 (7.5), Ce-SBA-15 (10), Ce-SBA-15 (12.5) and Ce-SBA-15 (15), respectively. Ce(IV) was spontaneously generated from  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  during the hydrothermal reactions [37]. The obtained Ce-SBA-15 samples were then scanned for high-angle PXRD patterns to find out whether or not any nanosized  $\text{CeO}_2$  phase is present in Ce-containing SBA-15 materials. As shown in Fig. 1, no  $\text{CeO}_2$  phase was observed in all Ce-SBA-15 samples. Unexpectedly, the  $\text{CeSiO}_4$



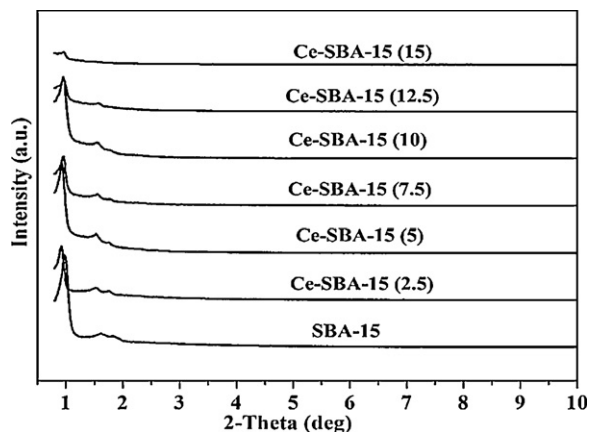
**Scheme 1.** Possible process of in situ formation of CeSiO<sub>4</sub> phase.

phase is observed both in as-synthesized and calcined samples. It is noticeable that when Ce/Si molar ratios increase from 2.5% to 10%, the diffraction intensity of CeSiO<sub>4</sub> phase in the corresponding Ce-SBA-15 samples is enhanced. However, when Ce/Si molar ratios are further increased to 12.5%, the diffraction pattern of CeSiO<sub>4</sub> phase disappeared (Fig. 1).

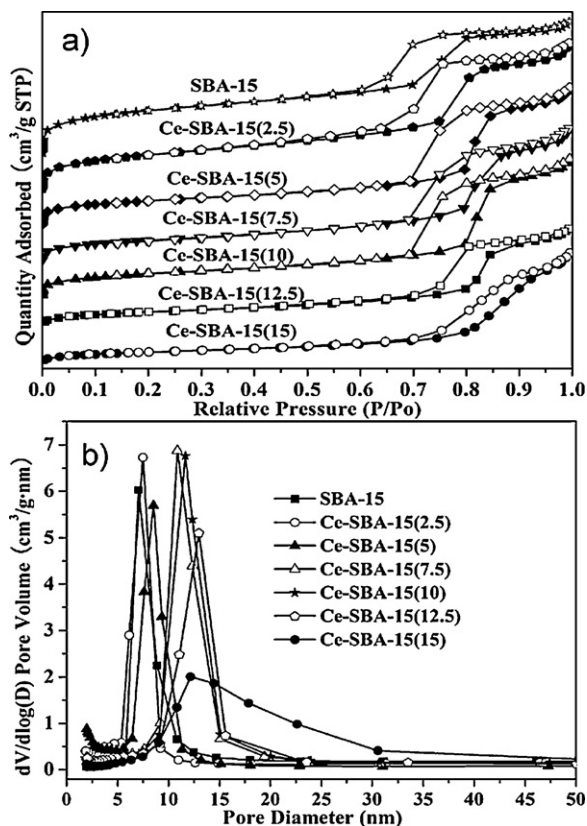
Generally, the mesoporous Ce-SBA-15 materials synthesized under strong acidic condition (pH < 1) have low amounts of cerium incorporated into SBA-15 [20]. However, lowering the acidity of the solution may decrease the hydrolysis rate of the cerium precursor to match that of the silicon precursor. This might enhance the interaction between the Ce–OH and Si–OH species in the synthesis gel. When decreasing H<sup>+</sup> concentration in the synthesis gel, the concentration of cerium hydroxyl species increases. Hence, under lesser concentration of H<sup>+</sup> in the synthesis gel at pH > 2, the structural and textural order of the mesoporous framework are also still maintained. Moreover, CeSiO<sub>4</sub> phase could only be formed in acidic media and more readily produced at higher temperatures [37], the weak acidic condition (pH 6) in reaction system which was adjusted with weak base (TEA) is helpful to forming CeSiO<sub>4</sub> phase. We think weak acidic condition not only synthesizes ordered mesoporous Ce-SBA-15, but leads to in situ formation of CeSiO<sub>4</sub> phase as well, as suggested process in Scheme 1. CeSiO<sub>4</sub> was confirmed to be a zircon-type structure with space group *I41/amd* and unit cell parameters: *a* = 6.9564(3), *c* = 6.1953(4) Å, as reported by Glasser [37,38].

### 3.2. Characterization of the Ce-SBA-15 samples

For low cerium-incorporated samples, the calcined Ce-SBA-15 materials retain its hexagonally packed porous structure as shown in the small angle PXRD patterns (Fig. 2). From the low-angle PXRD patterns, three peaks can be observed with the strongest one corresponding to (100) diffraction, together with two well-resolved (110) and (200) peaks. This suggested that these Ce-SBA-15 materials have highly ordered 2D hexagonal mesoporous structure (p6mm) and the introduction of cerium does not destroy the mesoporous structure of SBA-15 [39]. Conversely, for



**Fig. 2.** Small angle PXRD patterns of SBA-15 and Ce-SBA-15 samples.



**Fig. 3.** (a) Nitrogen adsorption/desorption isotherms and (b) pore-size distribution curves of SBA-15 and Ce-SBA-15 samples.

higher cerium-incorporated samples (Ce/Si molar ratio > 12.5%), the intensity of (100) diffraction becomes very weak, and (110) and (200) peaks essentially disappeared, implying ordered mesoporous structure is significantly destroyed for these samples. Moreover, after incorporating cerium, the (100) peak is shifted to lower  $2\theta$  values (Fig. 2). It can be explained by the distinction of atomic radius of Ce<sup>4+</sup> (1.06 Å) and Si<sup>4+</sup> (0.39 Å). Considering the Ce–O bond length is longer than that of Si–O, it can be speculated that cerium species has been incorporated into the mesoporous framework of SBA-15 [40].

As shown in Fig. 3, SBA-15 and Ce-SBA-15 exhibit similar N<sub>2</sub> adsorption/desorption isotherms of IV-type with an H1-type hysteresis loop of mesoporous materials. The profiles are the characteristic of mesoporous materials having cylindrical channels. Three well-distinguished regions of the adsorption isotherms (Fig. 3a) are obvious: (1) monolayer multilayer adsorption ( $P/P_0 = 0-0.5$ ); (2) capillary condensation ( $P/P_0 = 0.5-0.8$ ) and (3) multilayer adsorption on the outer surface ( $P/P_0 = 0.8-1.0$ ). A sharp inflection in the relative pressure ( $P/P_0$ ) between 0.5 and 0.8 corresponds to capillary condensation within uniform mesopores, and is a function of the pore diameter. The uniform pore size distribution is demonstrated by the sharpness of this step and displayed in the insets of Fig. 3b. However, Ce-SBA-15 (15) shows a wider pore size distribution, corresponding to its disordered mesoporous structure as demonstrated by PXRD pattern. The SBA-15 has a large BET surface area of 843.6 m<sup>2</sup>/g, high pore volume of 1.15 cm<sup>3</sup>/g, and moderate pore size of 6.3 nm, but Ce-SBA-15 materials possess lower BET surface area (Table 1). Interestingly, the BET surface area of the Ce-SBA-15 materials exhibits gradual decrease, when increasing the cerium content in materials (Table 1). Ce-SBA-15 materials also possess obviously large pore size compared with SBA-15 (Table 1). The larger pore size of Ce-SBA-15 materials after

**Table 1**

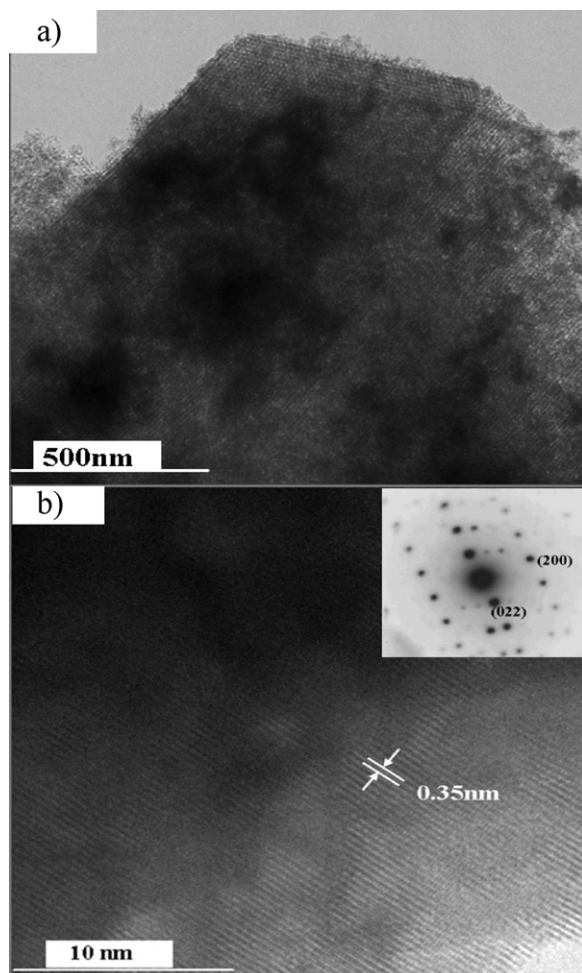
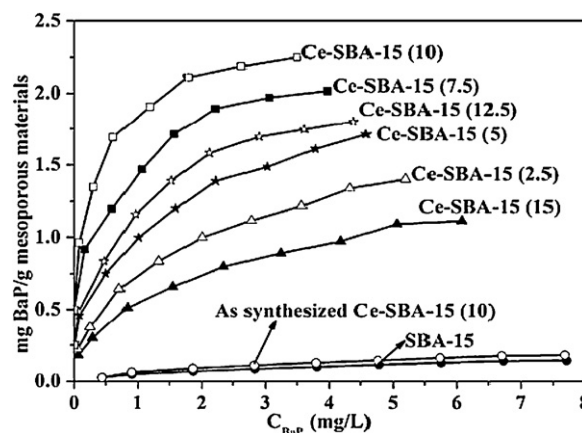
The physical–chemical properties of SBA-15 and Ce-SBA-15 samples.

Materials	$S_{\text{BET}}^a$ ( $\text{m}^2/\text{g}$ )	$V_p^b$ ( $\text{cm}^3/\text{g}$ )	$D_p^b$ (nm)
SBA-15	843.6	1.15	6.26
Ce-SBA-15 (2.5)	690.8	1.27	7.36
Ce-SBA-15 (5)	471.6	1.20	9.73
Ce-SBA-15 (7.5)	436.7	1.19	10.44
Ce-SBA-15 (10)	415.4	1.15	11.07
Ce-SBA-15 (12.5)	388.3	0.93	12.31
Ce-SBA-15 (15)	295.9	0.89	13.82

<sup>a</sup> The specific surface area was calculated by using the BET (Brunauer–Emmett–Teller) model.<sup>b</sup> The pore volume and pore size distributions were determined by the BJH (Barrett–Joyner–Halenda) method.

Ce(IV) functionalization should be attributed to the longer Ce–O bond length, because the atomic radius of  $\text{Ce}^{4+}$  (1.06 Å) is larger than that of  $\text{Si}^{4+}$  (0.39 Å). Low BET surface area of Ce-SBA-15 suggests  $\text{CeSiO}_4$  phase has highly filled in the mesoporous channels, which partly blocks the pore space of mesoporous channels [41].

The morphology of Ce-SBA-15 is depicted in Fig. 4. The TEM image displays that the mesoporous structure was retained for Ce-SBA-15 (10) sample. One can also observe the dark  $\text{CeSiO}_4$  phase supported on Ce-SBA-15 (10) sample from TEM micrograph (Fig. 4a). The pale yellow solid of Ce-SBA-15 sample also demonstrates the existence of  $\text{CeSiO}_4$  phase, because  $\text{CeSiO}_4$  itself is a pale yellow solid [37]. The HRTEM pattern of  $\text{CeSiO}_4$  phase in Ce-SBA-15 (10) is shown in Fig. 4b, which further supports

**Fig. 4.** TEM (a) and HRTEM (b) image of Ce-SBA-15 (10). The inset in (b) is the SAED of Ce-SBA-15 (10).**Fig. 5.** Adsorption curves of SBA-15 and Ce-SBA-15 mesoporous materials for BaP cyclohexane solutions at room temperature.

the single-crystalline nature of the particles. The interlayer distance was calculated to be  $\approx 0.35$  nm, which agrees well with the separation between the (200) lattice planes. The EDX spectrum (Fig. S1, in Supporting Information) indicates Ce-SBA-15 (10) sample is composed of Ce, O and Si elements.

### 3.3. The adsorption behavior of SBA-15 and Ce-SBA-15 materials for BaP

Initially, the room-temperature adsorption behavior of SBA-15 and Ce-SBA-15 materials for BaP solution in cyclohexane was investigated. It is obviously found that when Ce/Si molar ratios increase from 0% to 10%, the adsorption capacity of Ce-SBA-15 materials for BaP tends to increase (Fig. 5), however, when Ce/Si molar ratios are further increased to 12.5% and 15%, the BaP adsorption capacities on these two materials decreased (Fig. 5). Particularly, Ce-SBA-15 (15) sample exhibits low adsorption capacity for BaP. Regardless of large surface area and moderate pore size, SBA-15 exhibits very low adsorption capacity for BaP. These experimental results indicate the adsorption interactions of SBA-15 and Ce-SBA-15 materials for BaP can not be attributed to the surface area or shape selectivity effects of these mesoporous materials, because the materials (from Ce-SBA-15 (2.5) to Ce-SBA-15 (10)) with low surface area show higher adsorption capacities than that SBA-15 itself with high surface area (Table 1). Furthermore, compared to Ce-SBA-15 materials, SBA-15 should possess good shape selectivity for BaP due to its small pore size (Table 1), but it exhibits very low adsorption capacity. Kuehl suggests that pore size should be large enough to allow PAHs diffusion along the mesoporous channels; nevertheless, it should also be small enough to provide a potential field that retains adsorbed molecules for shape selectivity [42]. Consequently, the adsorption interactions cannot effectively interpret higher adsorption capacities of some Ce-SBA-15 materials (from Ce-SBA-15 (2.5) to Ce-SBA-15 (12.5)), it must have other reason.

### 3.4. Room-temperature catalytic oxidation of benzo(a)pyrene

When using Ce-SBA-15 (10) as adsorbent due to its highest adsorption capacity, an unexpected phenomenon was observed in the adsorption experiment: the adsorption system was gradually changed to orange and even red color during a short adsorption period at room temperature. According that adsorption equilibrium can be rapidly reached (achieving saturation adsorption with about 1 h) when using Ce-SBA-15 (10) as adsorbent (Fig. 6), the images of equilibrium systems with different initial BaP concentrations are taken at room temperature (Fig. 7a). One can see that colors of the different equilibrium systems are gradually changed to orange

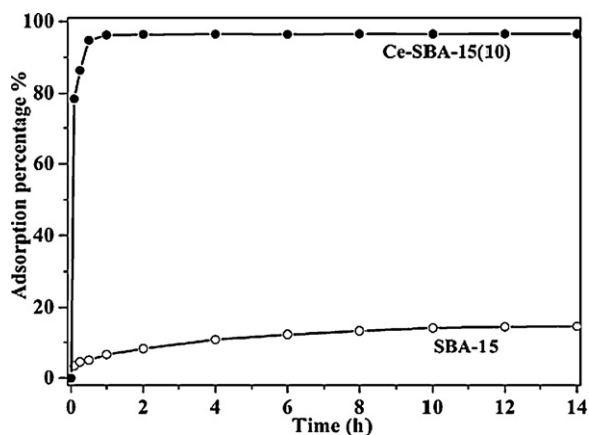
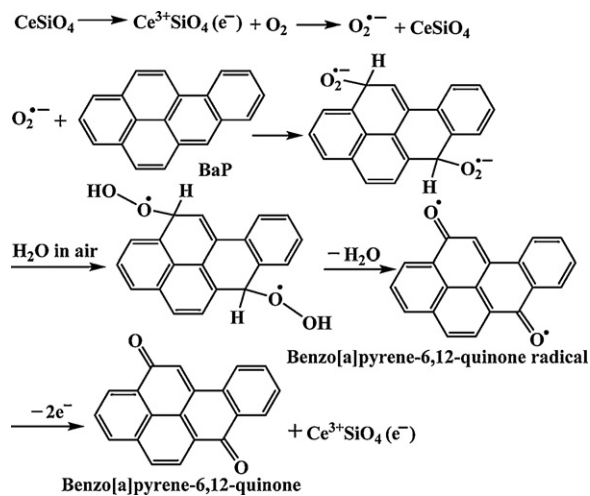


Fig. 6. Adsorption kinetics of BaP cyclohexane solutions ( $C_0 = 3 \text{ mg/L}$ ) on SBA-15 and Ce-SBA-15 (10) mesoporous materials at room temperature.

and even red with increasing initial BaP concentrations. Such color changes should be attributed to BaP transferring to corresponding quinone through catalytic oxidation by active  $\text{CeSiO}_4$  phase. Actually, BaP can be oxidized to quinone by cerium salt [43]. This transfer reaction is probably radical oxidation mechanism by in situ forming  $\text{O}_2^{\bullet-}$  under air condition at room temperature (Scheme 2). A control experiment with Ce-SBA-15 (10), BaP solution in cyclohexane and a radical scavenger (TEMPO) was carried out, the result shows the catalytic oxidation reaction was completely shut off (Fig. 8), because no red equilibrium system was observed when using TEMPO as a radical scavenger. This result indicates that the reaction involved radical intermediates as shown in Scheme 2.

Red equilibrium systems should derive from the formation of quinone. When BaP was transferred to corresponding quinone, molecular dipole was increased. As a result, quinone reveals higher affinity with mesoporous channels of Ce-SBA-15 (10), which further promotes BaP to be adsorbed and then to be transferred to quinone, giving rise to much higher adsorption capacities than that of SBA-15. On the other hand, when Ce/Si molar ratios exceed 12.5%, the corresponding material (Ce-SBA-15 (15)) exhibits low adsorption capacity, because there is no observed  $\text{CeSiO}_4$  phase in this material, consequently, it cannot effectively transfer BaP to quinone, leading to low adsorption capacity. The Ce-SBA-15 (15) sample still exhibits slightly higher adsorption capacity than that of SBA-15, attributable to low concentration  $\text{CeO}_2$  nanoparticles in



Scheme 2. Proposed mechanism for room-temperature catalytic oxidation BaP to benzo(a) pyrene-6,12-quinone by active  $\text{CeSiO}_4$ .

the Ce-SBA-15 (15) sample, although these  $\text{CeO}_2$  nanoparticles cannot be observed by PXRD. Although the as-synthesized Ce-SBA-15 (10) also contains  $\text{CeSiO}_4$  phase, it still exhibits very low adsorption capacity for BaP, because P123 templates occupy the channels that impede the adsorption of BaP. From above experimental results, we think Ce-SBA-15 materials, such as Ce-SBA-15 (7.5) and Ce-SBA-15 (10), first adsorb BaP, the adsorbed-BaP then is transferred to quinone, resulting in higher adsorption capacities. Among, catalytic oxidation by active  $\text{CeSiO}_4$  phase is a key factor to increase BaP adsorption capacities. Conversely, the materials without  $\text{CeSiO}_4$  phase (SBA-15 and SBA-15 (15)) reveal very low adsorption capacities for BaP which support catalytic oxidation by active  $\text{CeSiO}_4$  phase is a key factor; the as-synthesized Ce-SBA-15 (10) material that contains  $\text{CeSiO}_4$  phase, but possesses very small channels also exhibits very low adsorption capacity (Fig. 5) indicate the adsorption is initial process. In addition, the color changing extent of adsorption equilibrium systems with various materials is relative to content of  $\text{CeSiO}_4$  phase in the materials (Fig. S2). Because methanol has high affinity with quinone, Ce-SBA-15 (10) material offer ease of handling and purification through simple extraction of quinone by methanol (Fig. S3), giving rise to its recovery and recycling. In order to examine this possibility, we carried out adsorption and

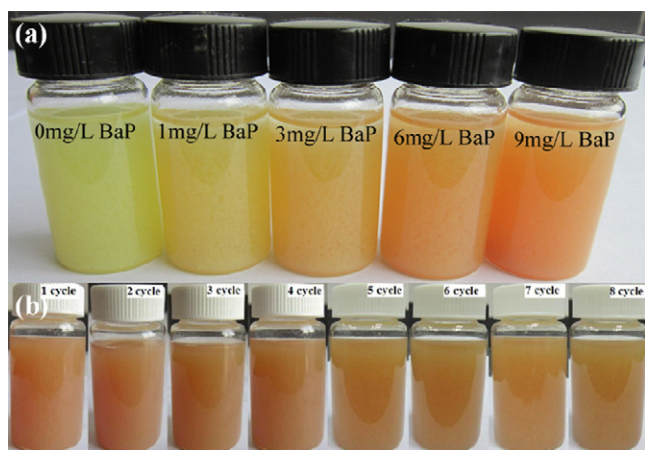
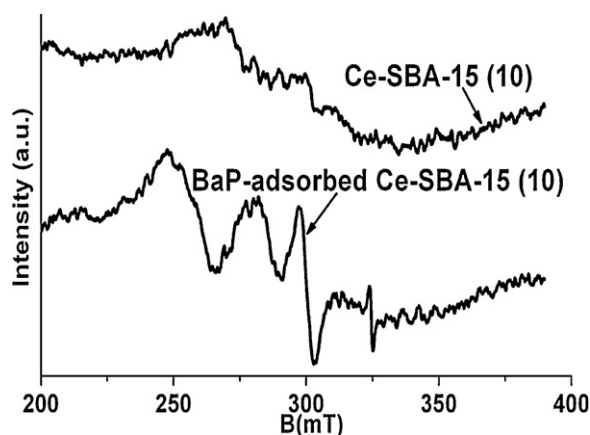


Fig. 7. Photographs of equilibrium systems of Ce-SBA-15 (10) with (a) different initial BaP concentrations and (b) initial BaP concentration of 9 mg/L for 6 recycling experiments. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)



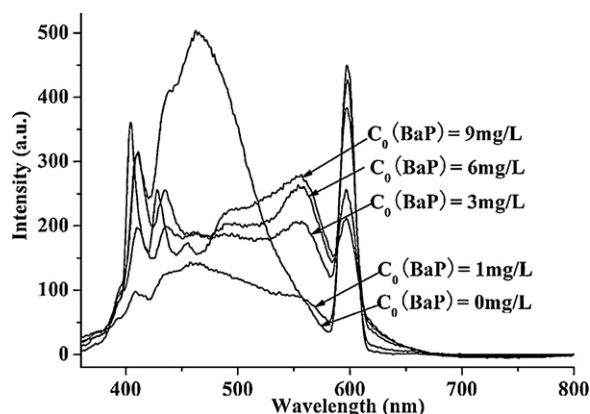
Fig. 8. Photographs of equilibrium systems of Ce-SBA-15 (10) without TEMPO (left) and with TEMPO (right). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)



**Fig. 9.** Solid-state EPR spectra of Ce-SBA-15 (10) and BaP-adsorbed Ce-SBA-15 (10) at room temperature (BaP-adsorbed Ce-SBA-15 (10) was separated from equilibrium system by filtration, washed with water and dried at 40 °C).

in situ catalytic oxidation reaction for 8 times with the same Ce-SBA-15 (10) material under the same condition. Before reuse, the quinone was extracted by methanol from BaP-adsorbed Ce-SBA-15 (10), the solid was separated by filtration, washed with methanol and finally dried at 150 °C under vacuum condition. The similar colors (Fig. 7b) of equilibrium systems for 8 cycles and the almost the same PXRD pattern of CeSiO<sub>4</sub> in Ce-SBA-15 (10) after reused 8 times indicate that Ce-SBA-15 (10) can be repeatedly used more than 8 times without apparently decreasing catalytic activity of CeSiO<sub>4</sub>.

The in situ forming quinone was further demonstrated by EPR, photoluminescence (PL), ESI-MS, IR and NMR. The solid-state EPR spectra were recorded for Ce-SBA-15 (10) and BaP-adsorbed Ce-SBA-15 (10) at room temperature (Fig. 9). No EPR signal for Ce-SBA-15 (10) is observed, however, BaP-adsorbed Ce-SBA-15 (10) exhibits two isotropic EPR signals centered at  $g=2.14$  and  $2.00$ , corresponding to Ce<sup>3+</sup> and quinone radical, respectively. The EPR results demonstrate radical oxidation mechanism as proposed above. Moreover, methanol extraction solution was EPR silent, implying it mainly exists as quinone, or quinone radical exists as diamagnetic ( $S=0$ )  $\pi$ -dimer [44]. On the other hand, when using TEMPO as a radical scavenger, such BaP-adsorbed Ce-SBA-15 (10) exhibits a symmetrical resonance EPR signal with  $g$ -value of 1.998 (Fig. S4), indicating a typical organic radical of TEMPO. Compared to PL spectrum of BaP in cyclohexane solution (Fig. S5), PL spectra of methanol extraction solutions with different initial BaP concentrations exhibit a new characteristic emission band at about 556 nm (Fig. 10), which are presumably ascribed to quinone-type molecule.



**Fig. 10.** Room-temperature PL spectra of methanol extraction solutions from BaP-adsorbed Ce-SBA-15 (10) with different initial BaP concentrations.

The quinone-type molecule in methanol extraction solution was also judged from IR (Fig. S6), ESI-MS (Fig. S7), and <sup>1</sup>H and <sup>13</sup>C NMR (Figs. S8 and S9). The IR absorption band of methanol extraction solution at about 1729 cm<sup>-1</sup> (marked by asterisk) is assigned to the stretching vibration of quinone carbonyl group. Even if it is difficult to obtain purified quinone-type molecule from methanol extraction solution, <sup>13</sup>C NMR displays signals with  $\delta$  values between 180 and 185 ppm, also indicative of the presence of quinone carbonyl group.

#### 4. Conclusion

In conclusion, we have discovered an active CeSiO<sub>4</sub> phase which was in situ formed during synthesis of Ce-SBA-15 mesoporous materials. Interestingly, at room temperature, BaP can be transferred to corresponding quinone catalyzed by this active CeSiO<sub>4</sub> phase through a radical oxidation mechanism. Such catalytic oxidation reaction also results in high adsorption capacities for BaP on Ce-SBA-15 materials. The catalytic oxidation BaP at room temperature makes such mesoporous materials promising candidates for potential applications in reducing the emissions of toxic BaP. The further extension of this work to reducing other PAHs is in progress.

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#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apcatb.2012.08.008>.

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